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Silica-Enhanced Sorbents for Dry Injection Removal of SO2 from Flue Gas

Acurex Corp., Research Triangle Park, NC

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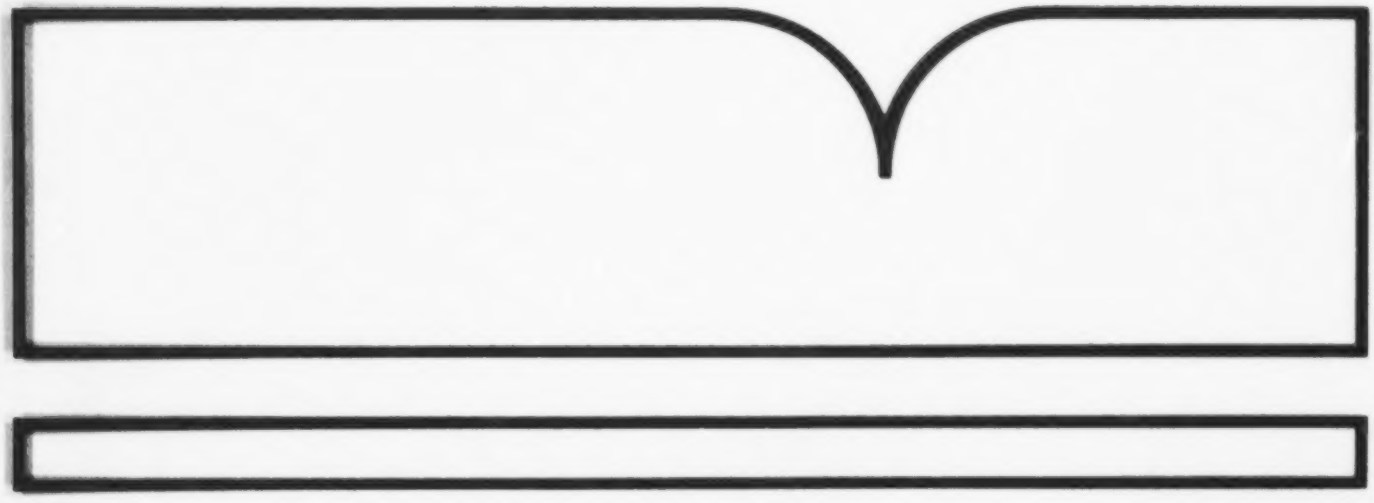

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16. ABSTRACT The paper gives results of tests of novel silica-enhanced lime sorbents in a bench-scale sand-bed reactor for their potential for SO2 removal from flue gas. Reactor conditions were: 64 C, relative humidity 60% (corresponding to an approach to saturation temperature of 10 C), and inlet SO2 concentration 500 or 1000 ppm. The sorbents were prepared by pressure hydration of CaO or Ca(OH)2 with siliceous materials at 100-230 C (101-2793 kPa) for from 15 min. to 4 h. Pressure hydration fostered the formation of a sorbent reactive with SO2 from flyash and Ca(OH)2 in a much shorter time than did atmospheric hydration. The conversion of Ca(OH)2 in the sand-bed reactor increased with the increasing weight ratio of flyash to lime and correlated well with B. E. T. surface area, increasing with increasing surface area. The optimum temperature range for the pressure hydration of flyash with Ca(OH)2 was 110-160 C. The pressure hydration of diatomaceous earth with CaO did not offer significant reactivity advantages over atmospheric hydration; however, the rate of enhancement of Ca(OH)2 conversions was much faster with pressure hydration. SEM and x-ray diffraction studies showed solids of different morphology with different flyash/lime ratios and changing conditions of pressure hydration.

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ABSTRACT

Novel silica-enhanced lime sorbents were tested in a bench-scale sand-bed reactor for their potential for SO_2 removal from flue gas. Reactor conditions were 64°C (147°F), relative humidity of 60% [corresponding to an approach to saturation temperature of 10°C (18°F)], and inlet SO_2 concentration of 500 or 1000 ppm. The sorbents were prepared by pressure hydration of CaO or $Ca(OH)_2$ with siliceous materials at 100°C (101 kPa) [212°F (14.7 psi)] to 230°C (2793 kPa) [446°F (405 psi)] for 15 min. to 4 h. Pressure hydration fostered the formation of a sorbent reactive with SO_2 from flyash and $Ca(OH)_2$ in a much shorter time than did atmospheric hydration. The conversion of $Ca(OH)_2$ in the sand-bed reactor increased with the increasing weight ratio of flyash to lime and correlated well with B.E.T. surface area, increasing with increasing surface area. The optimum temperature range for the pressure hydration of flyash with $Ca(OH)_2$ was between 110 and 160°C (230 and 320°F). The pressure hydration of diatomaceous earth with CaO did not offer significant reactivity advantages over atmospheric hydration; however, the rate of enhancement of $Ca(OH)_2$ conversions was much faster with pressure hydration. Scanning electron microscope (SEM) and x-ray diffraction studies showed solids of different morphology with different flyash/lime ratios and changing conditions of pressure hydration.

INTRODUCTION

Research on novel silica-enhanced calcitic sorbents for dry injection removal of SO_2 from flue gas has been conducted in EPA's Air and Energy Engineering Research Laboratory (AEERL). It has been demonstrated that these sorbents provide significantly higher conversion of $Ca(OH)_2$ compared with conventional $Ca(OH)_2$. The results of bench-scale experiments have been confirmed[1,2] using AEERL's 58 cfm (100 m^3/h) pilot plant and EPRI's 4000 cfm (6900 m^3/h) Arapahoe pilot plant.[3] Several materials were tested as a source of silica for the reaction with lime to form calcium silicate hydrates as a result of a pozzolanic reaction between these two reagents. Five different flyashes,[2,4] diatomaceous earth,[1] and montmorillonitic clays[2] were used, and all proved to be very effective promoters of $Ca(OH)_2$ conversion during the reaction with SO_2. To enhance the utilization of $Ca(OH)_2$, the siliceous materials had to be slurried with $Ca(OH)_2$ under favorable conditions of time and temperature. For flyash -- which is the most abundant source of silica when considering power plant flue gas desulfurization (FGD) -- to promote the conversion of $Ca(OH)_2$, long hydration time and above-ambient temperature were needed during the preparation of the sorbent. Additionally, it was found[4] that high weight ratios of flyash to $Ca(OH)_2$ were needed to increase the conversion, which increased with increasing ratios. A way to commercially obtain a high ratio of flyash to $Ca(OH)_2$ is to recycle the catch from the particulate control device downstream of the injection point. Unfortunately, this can deteriorate the performance of this device by the increased particulate loading in the gas.

To decrease the weight ratio of flyash to $Ca(OH)_2$ and to reduce the sorbent preparation time, pressure hydration instead of atmospheric hydration was tested. The term "hydration" is used here even though hydrated lime [$Ca(OH)_2$] and not quicklime (CaO) was reacted with a siliceous material. However, as a result of this reaction, the calcium silicate hydrates formed are usually highly hydrated.

Pressure hydration is used commercially to hydrate dolomitic limes (CaO + MgO), since it allows hydration of MgO which is impossible to hydrate completely during reasonable time under atmospheric conditions. At atmospheric pressure, high calcium limes hydrate from within minutes to an hour.[5] Very few dolomitic limes can be substantially hydrated at atmospheric pressure when the so-called retention method is used for periods from 10 to 24 h, permitting partial hydration of the MgO component of a dolomitic lime. Conditions of high pressure and temperature occurring in the pressure hydrator significantly increase the reaction rate of MgO, so that dolomitic lime can be fully hydrated within time periods typical for high calcium limes. It may be that the use of pressure hydration could also increase the reaction rate of

flyash, which was found[4] to be a rate limiting step during the formation of novel flyash-enhanced lime sorbents.

To address the problem of handling large quantities of solids when using high flyash to $Ca(OH)_2$ ratios to produce highly reactive sorbent, sources of silica other than flyash were tested. When commercially available diatomaceous earth or montmorillonite was substituted for flyash, a more reactive mixture of lower bulk solids content could be obtained. However, these materials presented two major disadvantages compared with flyash: higher cost [diatomaceous earth and montmorillonite cost $110 and $88 per tonne ($100 and $80 per ton), respectively] and availability (limited to the Western U.S.).

This paper describes bench-scale experimental work to produce reactive sorbents highly suited for dry SO_2 control. It focusses primarily on the pressure hydration of flyash or diatomaceous earth with $Ca(OH)_2$ with the aim of reducing the time of hydration and the weight ratio of siliceous materials to lime.

HYDROTHERMAL REACTION OF LIME AND SILICA -- PREVIOUS WORK

Hydrothermal reactions of lime and silica (amorphous silica was used) were studied[6] in the temperature range from 110 to 300°C (230 to 572°F) for a molar ratio of calcium to silica of 1:1. At 110°C (230°F) Type I calcium silicate hydrates (which may vary in composition in the range from $CaO \cdot SiO_2 \cdot nH_2O$ to $3CaO \cdot 2SiO_2 \cdot nH_2O$) appeared to be the final product of reaction. At higher temperatures, it was obtained as an intermediate product. At 135-180°C (275-356°F), $CaO \cdot SiO_2 \cdot H_2O$ was produced, while at 160-300°C (320-572°F) xonotlite ($4CaO \cdot 4SiO_2 \cdot 0.2H_2O$) was formed.

In another study,[7] molar ratios of CaO to SiO_2 varying from 1:2 to 3:1 were investigated for the temperature range of 50-1000°C (122-1832°F). At a molar ratio of CaO to SiO_2 of 2:3, gyrolite ($2CaO \cdot 3SiO_2 \cdot 2H_2O$) was formed in the temperature range 140-200°C (284-392°F). With a molar ratio of 2:1, α-$2CaO \cdot SiO_2 \cdot 10H_2O$ (α-dicalcium silicate) was formed instead of gyrolite in the temperature range from 120 to 160°C (248 to 320°F). It was observed during the above study[7] that the hydrates contained molecular water when formed under temperatures up to about 150°C (302°F). Above that temperature, they could contain less molecular water but some ionic hydroxyl. Above 300-600°C (572-1112°F) (depending on the ratio of Ca/Si: lower temperature for the ratio of 2:3, higher for 2:1), the products formed were anhydrous. Some work was done using diatomaceous earth.[8] These researchers reported the formation of Type I calcium silicate hydrates (Ca/Si molar ratio of the product less than 1.5) when lime and diatomaceous earth were pressure-hydrated at 175°C (347°F) for 2 h with the starting molar ratio of CaO/SiO_2 in the range of 1:1 to 4:3. It should be pointed out that both studies[7,8] were conducted under equilibrium conditions and used pure substrates (amorphous silica). During the early stages of formation (several hours) of interest in this study, a mixture of calcium silicate hydrates of different Ca/Si ratios and varying waters of hydration are probably formed. The amount of combined moisture in the sorbent is dependent on the temperature of pressure hydration. The ratio of Ca/Si in the final product depends on the starting weight ratio of

siliceous-material-to-lime and on the temperature-dependent availability of active silica.

The sorbents should have high surface area and molecular moisture for enhanced reactivity in the dry injection flue gas desulfurization (FGD) process. The water of hydration, if released on contact with hot gas, will provide moisture for enhancing SO_2 capture by $Ca(OH)_2$. Additionally, releasing the water of hydration can expose more sorbent particle pores and create new surface area.

EXPERIMENTAL

APPARATUS

The reactivity of sorbents was evaluated in a "sand-bed reactor" designed to simulate conditions in a fabric filter. The experimental apparatus, shown in Figure 1, has been explained in greater detail elsewhere.[9] In this study, it was used as a screening tool for sorbents to be tested in a small pilot plant. The sample of sorbent dispersed in sand (1 g of sorbent in 40 g of sand) was contacted with SO_2-containing nitrogen under controlled temperature and relative humidity (i.e., approach to saturation). One hour was arbitrarily selected as the residence time of the sorbent in the reactor during the exposure to SO_2. This choice of residence time was based on typical baghouse cleaning cycles from 30 min. to several hours, depending on solids loading and characteristics as well as flow conditions and filter material.

The experiments were performed at 64°C (147°F) and a relative humidity of 60% [corresponding to an approach to saturation of 10°C (18°F)]. The nominal SO_2 concentration was 500 or 1000 ppm [1.33 or 2.67 g SO_2/m^3 at 20°C (68°F)].

SAMPLE PREPARATION AND EVALUATION

Sample preparation consisted of batch pressure hydration of the siliceous material/lime mixture and drying of the sample. A stainless steel hydrator of 300 ml (18.3 $in.^3$) capacity was used as a pressure hydrator. Initially, desired amounts of siliceous material, lime, and water were all put into the cold reactor. The hydrator was then sealed and heated to the desired temperature. Since it usually took about 20 min. for the hydrator to reach the desired temperature/pressure, it was apparent that this period would affect determining the true effect of hydration time for short hydration times (15, 30, 60 min.). A new procedure, rapid heating,[10] was therefore employed, as shown in Figure 2. Dry siliceous materials and lime (reactants) were put into the cold pressure hydrator, and the desired amount of water was poured into a 300-ml high pressure sampling cylinder. The injection valve in the line connecting the sampling cylinder with the pressure hydrator was closed, and the sampling cylinder was pressurized with nitrogen to about 345 kPa (50 psi) higher than the vapor pressure of water at the experimental temperature. The pressure hydrator was then heated electrically, controlled by a thermocouple inside the hydrator. When the temperature reached the desired value, the injection valve was opened and water was instantaneously injected from the sampling cylinder into the hydrator containing dry reactants and evaporated there. After the water injection/evaporation was completed

(monitored by the pressure gauge), the injection valve was closed and the sampling cylinder was disconnected. Throughout the hydration period, the sample was vigorously stirred. After completion of the hydration run, the injection valve was opened to depressurize the hydrator via steam release under a ventilated hood. The sample was taken from the reactor and microwave-dried for 5 min. to ensure its dryness. This method was used for testing the effectiveness of the short time pressure hydration.

The reactivity of the sorbents with SO_2 is expressed in this paper as "conversion," defined as the ratio of the total number of mols of SO_2 reacted after 1 h to the number of mols of $Ca(OH)_2$ initially in the sorbent. The reactivity of reagent grade $Ca(OH)_2$ (Fisher C-97) for a residence time of 1 h in the sand-bed reactor was the baseline for all work reported here. Using simulated flue gas containing 1000 ppm SO_2 at a temperature of 64°C (147°F) and 60% relative humidity [approach to saturation, Δt_s, of 10°C (18°F)], 1 g of reagent grade $Ca(OH)_2$ converted 0.17 mol SO_2/mol $Ca(OH)_2$ after a 1-h exposure.

Since siliceous materials investigated here are composites and may contain different amounts of available silica (active silica) for the reaction with lime, the siliceous material-to-lime weight ratio is used throughout this paper, rather than the molar ratio of silica to calcium. Different amounts of siliceous materials with different SiO_2 content would be needed to obtain a constant molar ratio of silica to calcium when activating a unit amount of lime. For example, to activate 10 g of $Ca(OH)_2$ with siliceous material at a molar ratio of SiO_2 to CaO of 1, 16.2 g of flyash with 50% SiO_2 content or 9.7 g of diatomaceous earth with 87% SiO_2 content would be needed. Assuming that both sorbents would yield the same conversion of $Ca(OH)_2$, 1.33 times more flyash/$Ca(OH)_2$ than of diatomaceous earth/$Ca(OH)_2$ sorbent would be needed to achieve the same degree of removal of SO_2 by both materials. While the molar ratio of silica to lime would be 1:1 in both cases, the information about the amount of sorbent would be contained in the weight ratio of siliceous-material-to-lime parameter, which would be 1.6:1 and 1:1 for flyash/$Ca(OH)_2$ and diatomaceous earth/$Ca(OH)_2$ sorbents, respectively.

The morphology of the samples was characterized using a scanning electron microscope (SEM). The crystalline phases were detected with an x-ray diffractometer, and the B.E.T. surface area was analyzed using an automated analyzer.

PRESSURE HYDRATION OF FLYASH/LIME MIXTURES

EFFECT OF FLYASH-TO-$Ca(OH)_2$ WEIGHT

It was observed previously[1] that the conversion of $Ca(OH)_2$ increased with increased weight ratio of flyash to $Ca(OH)_2$ when atmospheric hydration was used. No significant increase of the conversion could be seen when samples at a weight ratio ranging from 1:1 to 5:1 were hydrated atmospherically at 90°C (194°F) for 4 h. During this work, pressure-hydrated sorbents with flyash-to-$Ca(OH)_2$ weight ratios ranging from 1:2 to 5:1 were investigated. Flyash from the Clinch River Power Plant in Carbo, VA, obtained from the burning of eastern bituminous coal and containing about 50% of SiO_2, was the silica source. Figure 3 shows the reactivity of the sorbent as a function of

flyash-to-$Ca(OH)_2$ weight ratio. All samples tested were prepared by pressure hydration at 150°C (476 kPa) [302°F (69 psi)] for 2 h at a water-to-solids ratio of 15:1 (6% solids in the slurry). The samples were then dewatered and dried. The resulting dry powdered sorbent was mixed with sand and exposed to 500 ppm SO_2 in the sand-bed reactor operated at 64°C (147°F) and 60% relative humidity [Δt_s = 10°C (18°F)]. As can be seen in Figure 3, conversion of $Ca(OH)_2$ in the sorbent increased with increasing flyash-to-$Ca(OH)_2$ weight ratio. The measured B.E.T. surface area for pressure-hydrated samples, shown in Figure 3, generally increased with increasing weight ratio of flyash to $Ca(OH)_2$. Shown for comparison, the results for samples which were prepared by atmospheric hydration at 90°C (194°F) for 4 h indicate the greater effect pressure hydration had on the reactivity of the sorbent. For example, when a flyash-to-$Ca(OH)_2$ weight ratio of 2.3:1 was used, the conversion was 0.19 and 0.42 mol SO_2/mol $Ca(OH)_2$ when atmospheric and pressure hydration at the conditions described above were used, respectively. Based on these results, flyash/$Ca(OH)_2$ mixtures prepared by pressure hydration at weight ratios of 1:1 and 2.3:1 were recommended for pilot plant testing in AEERL's 100 m^3/h (58 cfm) spray dryer/baghouse or humidification/dry-injection/baghouse system.

Also investigated was the effect of the time of pressure hydration of flyash and $Ca(OH)_2$ at the weight ratio of 2.3:1 on the conversion of $Ca(OH)_2$ in the sand-bed reactor. The results are presented in Figure 4. The conversion for the pressure-hydrated mixture at 150°C (476 kPa) [302°F (69 psi)] followed the trend observed earlier for atmospheric-hydrated mixtures. This trend indicated that, for a constant weight ratio of flyash to $Ca(OH)_2$ and a constant temperature of hydration, the conversion of $Ca(OH)_2$ increased with increased time of hydration. For pressure hydration at 180°C (1000 kPa) [356°F (145 psi)] and 230°C (2793 kPa) [446°F (405 psi)] and with reactants at the same weight ratio, a maximum $Ca(OH)_2$ conversion occurred after 4 and 1 h, respectively. This phenomenon was probably due to the fact that all silica available for the reaction with lime (active silica) was used, and more rapidly at 230°C (446°F) than at 180°C (356°F). Similar behavior was observed when flyash and $Ca(OH)_2$ at a weight ratio of 1:1 were pressure-hydrated at 120 and 150°C (248 and 302°F). These results are presented in Figure 5. Maximum conversions of $Ca(OH)_2$ of 0.38 mol SO_2/mol $Ca(OH)_2$ after 1 h and 0.45 mol SO_2/mol $Ca(OH)_2$ after 2 h were observed for sorbents pressure-hydrated at 150 and 120°C (302 and 248°F), respectively. No enhancement of conversion above the baseline of 0.17 mol SO_2/mol $Ca(OH)_2$ occurred when the mixture of flyash and $Ca(OH)_2$ at a weight ratio of 1:1 was hydrated atmospherically for a period ranging from 1 to 5 h.

Comparison of atmospheric hydration reactivity data with recent results obtained for sorbents which were pressure-hydrated (Figures 4 and 5) clearly shows that a significant decrease of time of hydration is possible when pressure rather than atmospheric hydration is used. Atmospheric hydration at 90°C (194°F) for 8 h was required to enhance the conversion of $Ca(OH)_2$ up to 0.35 mol SO_2/mol $Ca(OH)_2$, when the weight ratio of flyash to $Ca(OH)_2$ was 2.3:1. The same conversion was achieved for the same reactants and weight ratio after they had been pressure-hydrated at 150°C (69 psi) [302°F (476 kPa)] for 1 h. The effect of pressure hydration on the conversion of $Ca(OH)_2$ is even more dramatic when the flyash-to-$Ca(OH)_2$ weight ratio is 1:1 instead of 2.3:1. A conversion as high as 0.45 mol SO_2/mol $Ca(OH)_2$ was observed after 2 h of pressure hydration at 120°C (200 kPa) [248°F (29 psi)].

Even after a short residence time of 15 min. at 120°C (248°F), it was possible to achieve a $Ca(OH)_2$ conversion of 0.25 mol SO_2/mol $Ca(OH)_2$.

EFFECT OF TEMPERATURE

To investigate the effect of hydration temperature on the reactivity of $Ca(OH)_2$, experiments were performed on sorbents prepared with flyash-to-$Ca(OH)_2$ weight ratios of 2.3:1 and 1:1 by pressure hydration for 4 h at temperatures ranging from 100°C (101 kPa) [212°F (14.7 psi)] to 230°C (2793 kPa) [446°F (405 psi)]. The sand-bed reactor results are shown as solid lines in Figure 6. When a weight ratio of flyash to $Ca(OH)_2$ of 2.3:1 was used, the conversion was a maximum of 0.46 mol SO_2/mol $Ca(OH)_2$ for sorbent pressure-hydrated at 150° (476 kPa) [302°F (69 psi)]. A further increase of the hydration temperature resulted in a gradually decreasing conversion, reaching the baseline value of 0.17 mol SO_2/mol $Ca(OH)_2$ at 230°C (2793 kPa) [446°F (405 psi)]. The decreasing conversion of $Ca(OH)_2$ with temperature in the range from 150 to 230°C (302 to 446°F) is probably caused by the formation of another phase, compared with the range from 100 to 150°C (212 to 302°F). Literature data[7] indicate that calcium silicates with significantly less molecular water may be formed in the 150 to 230°C (302 to 446°F) temperature range. However, the results (solid lines) in Figure 6 are somewhat biased in that the observed maximum conversion at a given temperature might have been different from values presented for the 4-h pressure hydrations. For example when using a flyash-to-$Ca(OH)_2$ weight ratio of 2.3:1, the maximum conversion of $Ca(OH)_2$ at 230°C (2793 kPa) [446°F (405 psi)] was 0.33 mol SO_2/mol $Ca(OH)_2$ for sorbent hydrated for 1 h. The conversion of sorbent prepared at the same weight ratio of flyash to $Ca(OH)_2$, but pressure hydrated at 230°C (446°F) for 4 h (value shown in Figure 6), was much lower [0.18 mol SO_2/mol $Ca(OH)_2$] for the reasons discussed earlier. When considering the effect of temperature, the maximum values of conversion at a given temperature must be considered to compensate for the time/temperature dependence of conversion. The maximum values for the range of 180-230°C (356-446°F) are presented as broken lines in Figure 6. The values for the 150-180°C (302-356°F) range are identical with those for the 4-h pressure hydrations. As can be seen, the maximum values of conversion somewhat offset the effect of increasing temperature. However, the optimum temperature of pressure hydration of flyash and $Ca(OH)_2$ at the weight ratio of 2.3:1 seems to be 150°C (302°F), with conversion decreasing for hydrations in the range from 150 to 230°C (302 to 446°F).

PRESSURE HYDRATION OF DIATOMACEOUS-EARTH/LIME MIXTURES

Previous work[1] indicated that diatomaceous earth was a more reactive source of silica than flyash and that lower siliceous-material-to-lime weight ratios were needed to activate lime for the removal of SO_2. The present work included pressure hydration of diatomaceous-earth/CaO mixtures at 150 and 230°C (476 and 2793 kPa) [302 and 446°F (69 and 405 psi)] for moderate times of 1 and 1.25 h, respectively. The diatomaceous earth used was Filter Cel (Johns-Manville Products Corporation), having about 87% SiO_2. The results for these mixtures are shown in Figure 7 for both pressure and atmospheric hydration. For the majority of conditions tested, no significant increase in conversion of $Ca(OH)_2$ was achieved by pressure hydration. Only at a weight ratio of Filter Cel to CaO of 1:1, the conversion of $Ca(OH)_2$ increased from about 0.6 mol SO_2/mol $Ca(OH)_2$ for a sorbent atmospherically hydrated at 90°C

(194°F) for 4 h to 0.76 mol SO_2/mol $Ca(OH)_2$ for a sorbent pressure hydrated at 150°C (302°F) for 1 h. However, the rate of enhancement of $Ca(OH)_2$ conversion was much faster when pressure hydration was used. It took about 1 and 4 h to produce a sorbent of comparable reactivity when pressure and atmospheric hydration were used, respectively. The insignificant difference between conversions for sorbents prepared by atmospheric and pressure hydration may be because diatomaceous earth, being much more reactive than flyash, reacts more quickly with lime than does flyash. If this is the case, most of the silica would react with lime under atmospheric hydration conditions, which are achieved prior to pressure hydration under constant volume heating. Some enhancement may be possible if diatomaceous earth and lime are pressure hydrated with additives, as described in the literature.[11]

DISCUSSION

Data presented above indicate that an enhanced conversion of $Ca(OH)_2$ is possible within a feasible time period when pressure hydration is used instead of atmospheric hydration in preparing siliceous-material/lime sorbents. Contrary to what was observed during experimental work with atmospheric hydration of flyash with $Ca(OH)_2$, conversion of $Ca(OH)_2$ in the sand-bed reactor did not always increase with the time of pressure hydration for a given temperature. Probably, because reactive silica was used rapidly (as the result of high temperature/pressure conditions), the formation of calcium silicate hydrate which is reactive with SO_2 was stopped, and it may be that this hydrate later recrystallized into a less reactive one having a lower surface area and less molecular water.

The correlation of the conversion of $Ca(OH)_2$ in the sand-bed reactor and B.E.T. surface area of the flyash/$Ca(OH)_2$ samples pressure-hydrated at different conditions of weight ratios of flyash to $Ca(OH)_2$, time, and temperature is shown in Figure 8. This figure shows that the conversion of $Ca(OH)_2$ in the sand-bed reactor correlated quite well with the measured B.E.T. surface area and that conversion increased with increasing surface area of the sorbent. However, considerable data scatter in the conversion of $Ca(OH)_2$ in the sand-bed reactor occurred for samples with B.E.T. surface areas in the range from 5 to 10 m^2/g. Probably, a more reactive phase of calcium silicate hydrate was formed at the weight ratio of flyash to $Ca(OH)_2$ of 2.3:1 than at 1:1. This was manifested by the fact that, for the same surface area, more $Ca(OH)_2$ was converted in the sand-bed reactor for the sorbent produced by the pressure hydration of flyash and $Ca(OH)_2$ at a weight ratio of 2.3:1 rather than at 1:1. For example, the expected conversion of $Ca(OH)_2$ in the sand-bed reactor would be about 0.35 and about 0.15 mol SO_2/mol $Ca(OH)_2$ for sorbents with a surface area of 5 m^2/g which were produced by pressure hydration of substrates at weight ratios of 2.3:1 and 1:1, respectively. Higher surface area sorbents were generally produced when a flyash-to-$Ca(OH)_2$ weight ratio of 2.3:1 was used rather than 1:1. The highest B.E.T. surface areas measured for sorbents prepared by pressure hydration at weight ratios of 2.3:1 and 1:1 were 29 and 14 m^2/g, respectively.

Three results for the sorbents prepared at a weight ratio of flyash to $Ca(OH)_2$ of 2.3:1 by pressure hydration at 230°C (2793 kPa) [446°F (405 psi)] do not correlate with the other results at this ratio. This seems to confirm

a literature report[7] that, at such high temperature, anhydrous compounds (i.e., with small amounts of molecular water) are formed.

The development of sorbent surface area when pressure-hydrating flyash with $Ca(OH)_2$ is shown in Figures 9 and 10. Figure 9 shows a sample of flyash and $Ca(OH)_2$ pressure-hydrated at 150°C (476 kPa) [302°F (69 psi)] for 15 min. This sorbent had a B.E.T. surface area of 4 m^2/g and in the sand-bed reactor had a conversion of 0.17 mol SO_2/mol $Ca(OH)_2$. Flyash particles with quite smooth surfaces can be seen in Figure 9, as well as big chunks of $Ca(OH)_2$, indicating that the reaction of flyash with $Ca(OH)_2$ has hardly started. Figure 10 is quite different, showing a sorbent with the same weight ratio and pressure-hydrated at the same temperature but for a longer period, 4 h. In this case, the measured B.E.T. surface area was 21 m^2/g, and the conversion of $Ca(OH)_2$ in the sand bed was 0.46 mol SO_2/mol $Ca(OH)_2$. No separate particles of $Ca(OH)_2$ and flyash can be seen in this sorbent; instead, a very well developed gel-like amorphous surface is evident in Figure 10, probably a very thin layer, since flyash particles can be seen underneath.

Figure 11 depicts the sorbent pressure hydrated at a weight ratio of flyash to $Ca(OH)_2$ of 2.3:1 at 230°C (2793 kPa) [446°F (405 psi)] for 4 h. Even though the measured surface area was 17 m^2/g, the conversion of $Ca(OH)_2$ in the sand-bed reactor was only 0.16 mol SO_2/mol $Ca(OH)_2$. When comparing Figures 10 and 11, different morphologies of the products are evident. Instead of the gel-like amorphous material shown in Figure 10, a framework of distinct needle-shaped crystals is seen in Figure 11. Probably the product in Figure 11 contains much less (or no) water of hydration then needed for the sorbent to be reactive with SO_2; therefore, this may explain why this sorbent demonstrated poor reactivity in the sand-bed reactor. This finding seems to be consistent with a report[12] which indicated that needle-like crystals of β-type calcium silicate were conversion products of α-type hydrates.

Still another morphology is evident in Figure 12 which shows the sample of flyash and $Ca(OH)_2$ pressure-hydrated at a weight ratio of 1:1 at 150°C (302°F) for 4 h. This sorbent had a B.E.T. surface area of only 4 m^2/g, and the conversion of $Ca(OH)_2$ in the sand-bed reactor was only 0.11 mol SO_2/mol $Ca(OH)_2$. Big (several micrometers) platelet crystals can be seen in Figure 12, and the flyash spherules in Figure 13 indicate a poorly developed surface that is probably responsible for the low reactivity of this sorbent.

The results of the morphology study presented in Figures 9 through 13 suggest that two factors are necessary for a sorbent to readily react with SO_2 under the conditions encountered during a cool-side FGD process: large sorbent surface area and amorphous surface structure. Both factors can be optimized by careful selection of the time/temperature conditions of pressure hydration for a selected flyash-to-$Ca(OH)_2$ weight ratio.

The results of a morphology study seem to be in good agreement with x-ray diffraction measurements presented in Figure 14. Vertical lines in Figure 14 denote two-theta angles where $Ca(OH)_2$ peaks would appear. Section A of Figure 14 is a diffraction pattern of flyash and $Ca(OH)_2$ dry-mixed at a weight ratio of flyash to $Ca(OH)_2$ of 2.3:1. Only peaks of $Ca(OH)_2$ and SiO_2 can be seen in this section (two major peaks of $Ca(OH)_2$ at 18 and 34° have intensities of about 250 and 350 counts per second, respectively). Section B

of Figure 14 is a diffraction pattern for a sorbent with a flyash to $Ca(OH)_2$ ratio of 2.3:1, pressure-hydrated at 150°C (476 kPa) [302°F (69 psi)] for 0.5 h. The intensity of $Ca(OH)_2$ peaks are significantly diminished compared with Section A (peaks at 18 and 34° were measured at 150 and 160 counts per second, respectively). This sorbent had a $Ca(OH)_2$ conversion of 0.32 mol SO_2/mol $Ca(OH)_2$ when exposed to SO_2 in the sand-bed reactor operated at the normal experimental conditions. Section C of Figure 14 is a diffraction pattern of a sorbent with a flyash-to-$Ca(OH)_2$ weight ratio of 2.3:1, pressure-hydrated at 150°C (476 kPa) [302°F (69 psi)] for 4 h. No peaks of $Ca(OH)_2$ can be seen in Section C and, when placed in the sand-bed reactor under normal operating conditions, this sorbent had a $Ca(OH)_2$ conversion of 0.46 mol SO_2/mol $Ca(OH)_2$. Comparison of Sections A, B, and C of Figure 14 indicates that the conversion of $Ca(OH)_2$ increases proportionally to the disappearance of $Ca(OH)_2$, probably because of its use in forming a new phase of silica-enhanced sorbent. Section D of Figure 14 is a diffraction pattern of a sorbent pressure-hydrated at 230°C (2793 kPa) [446°F (405 psi)] for 4 h. This sorbent had a flyash-to-$Ca(OH)_2$ weight ratio of 2.3:1, and its sand-bed reactor conversion of $Ca(OH)_2$ was 0.16 mol SO_2/mol $Ca(OH)_2$. A comparison of Sections C and D reveals that the hump at a two-theta angle of about 26° has an intensity of 40 and 20 counts per second, respectively. This hump is indicative of the amorphism of the sorbent and suggests that the sorbent pressure-hydrated at 150°C (476 kPa) [302°F (69 psi)] had a higher $Ca(OH)_2$ conversion in the sand-bed reactor than the one hydrated at 230°C (2793 kPa) [446°F (405 psi)] because its surface area was significantly more amorphous.

CONCLUSIONS

From the above study, the following conclusions may be drawn:

1. Very reactive sorbents for the dry injection removal of SO_2 from flue gas can be produced by the pressure hydration of flyash or diatomaceous earth with lime.

2. Pressure hydration fosters the formation of a flyash/$Ca(OH)_2$ sorbent which reacts with SO_2 in a much shorter time than does a similar sorbent prepared by atmospheric hydration.

3. Pressure hydration of diatomaceous earth with CaO does not offer significant advantages over atmospheric hydration in producing a reactive sorbent, probably because of the high reactivity of diatomaceous earth with lime even when atmospherically hydrated.

4. The conversion of $Ca(OH)_2$ in the sand-bed reactor generally did not monotonically increase with the time of hydration for a given temperature of pressure hydration. After all the reactive silica was used, recrystallization probably took place and resulted in solids of lower reactivity with SO_2.

5. The conversion of $Ca(OH)_2$ in the sand-bed reactor increased with the increasing weight ratio of flyash to lime. The conversion of $Ca(OH)_2$ was significantly enhanced by pressure hydration at low weight ratios of flyash to $Ca(OH)_2$ which were ineffective in promoting conversion of $Ca(OH)_2$ in sorbents prepared by atmospheric hydration.

6. An optimum temperature range for the pressure hydration of flyash with $Ca(OH)_2$ was found to be between 110 and 160°C (230 and 320°F). The reactivity of the sorbent gradually decreased when pressure hydration was in the range 180-230°C (356-446°F).

7. The conversion of $Ca(OH)_2$ in the flyash/$Ca(OH)_2$-derived sorbent correlated well with B.E.T. surface area, increasing with increasing surface area.

8. SEM and x-ray diffraction studies demonstrated the formation of solids of different morphology with different flyash/lime ratios and changing conditions of pressure hydration.

9. Comparison of sand-bed reactor data and SEM morphology studies indicates that both high surface area and high molecular water are necessary for the sorbent to be reactive with SO_2 at the flue gas conditions appropriate for the in-duct dry injection of sorbents.

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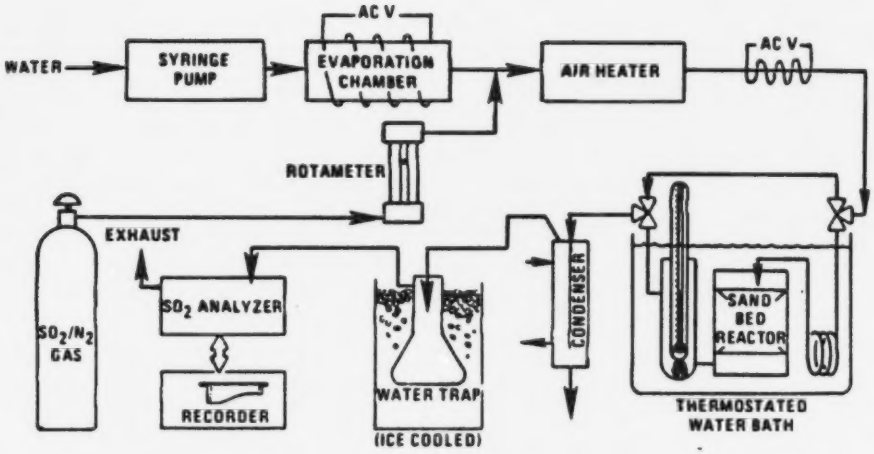

Figure 1. Sand-bed reactor for bench-scale evaluation of sorbents.

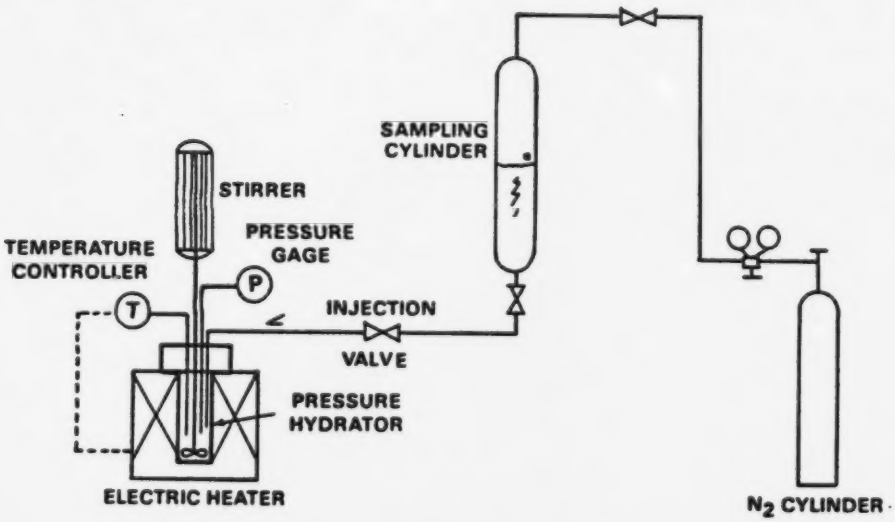

Figure 2. Experimental "rapid heating" apparatus for pressure hydration.

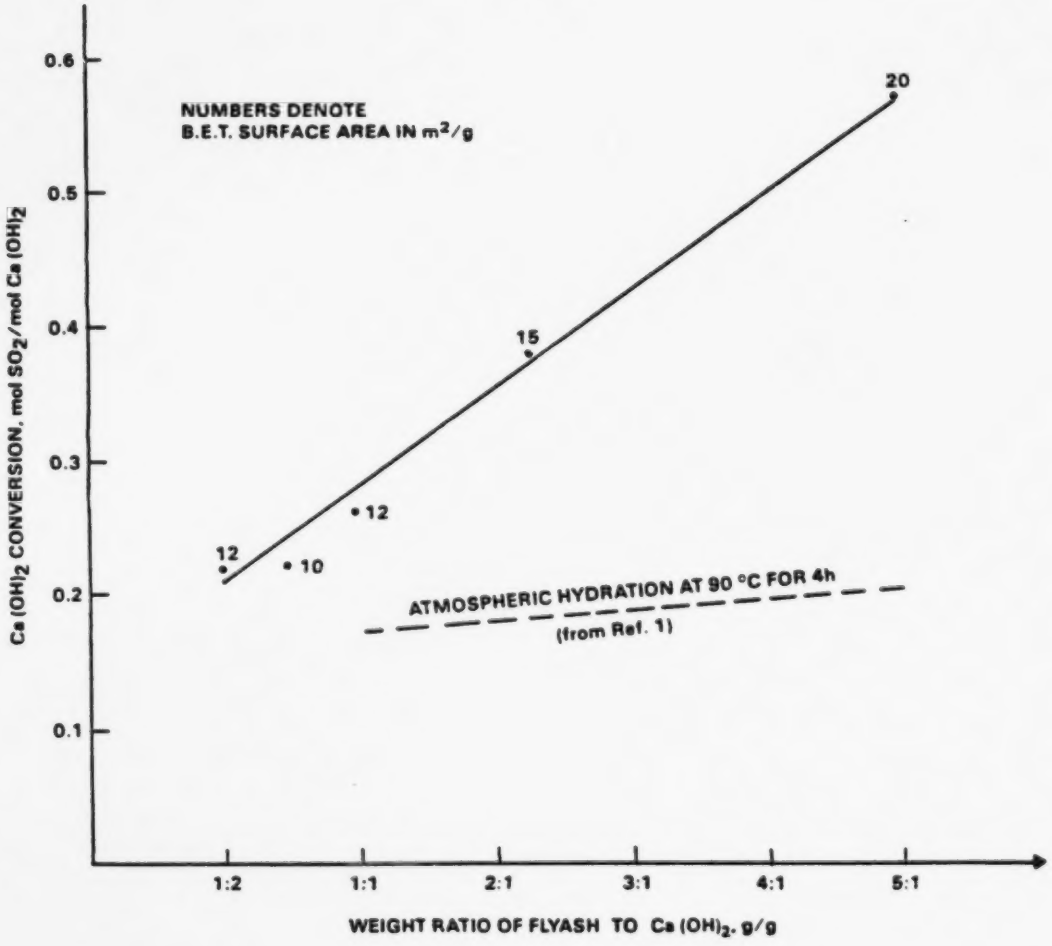

Figure 3. The effect of weight ratio of flyash to $Ca(OH)_2$ on the reactivity of pressure-hydrated sorbents [sand-bed reactor conditions: relative humidity 60%, temperature 64°C (147°F), SO_2 concentration 500 ppm; pressure hydrator conditions: temperature 150°C (302°F), 2 h].

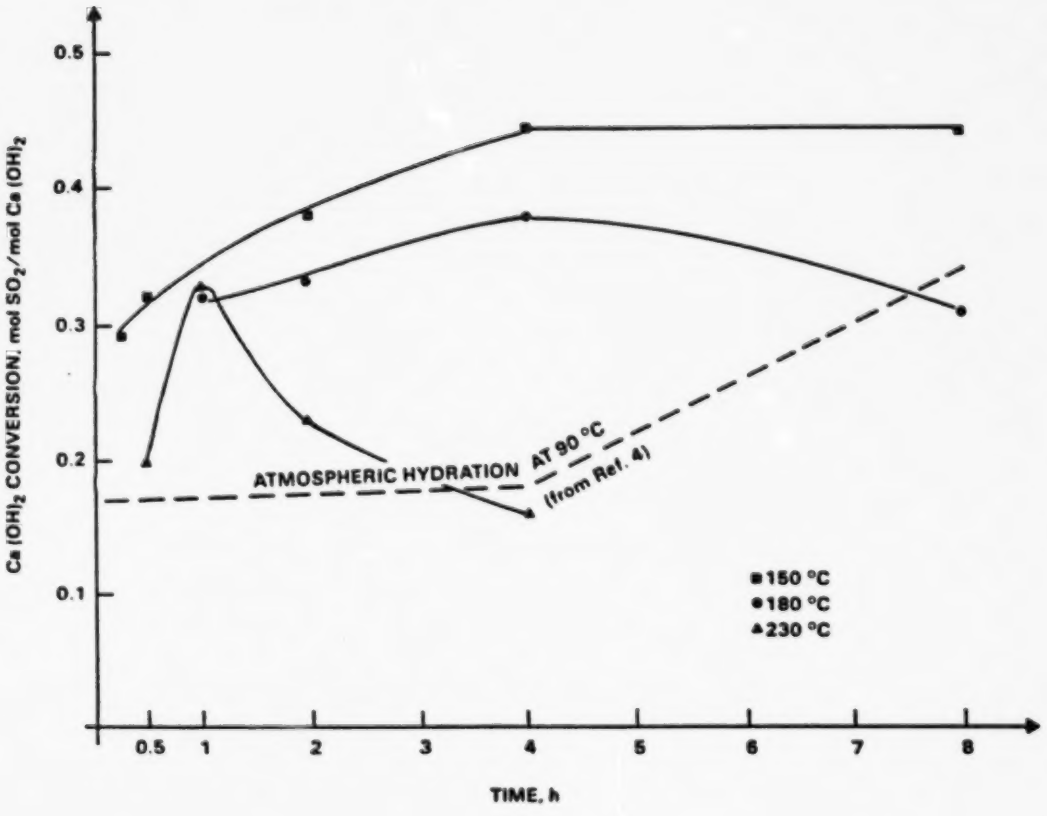

Figure 4. Combined time and temperature effects of pressure hydration on the reactivity of sorbent prepared at the weight ratio of flyash to $Ca(OH)_2$ of 2.3:1 (sand-bed reactor conditions the same as in Figure 3).

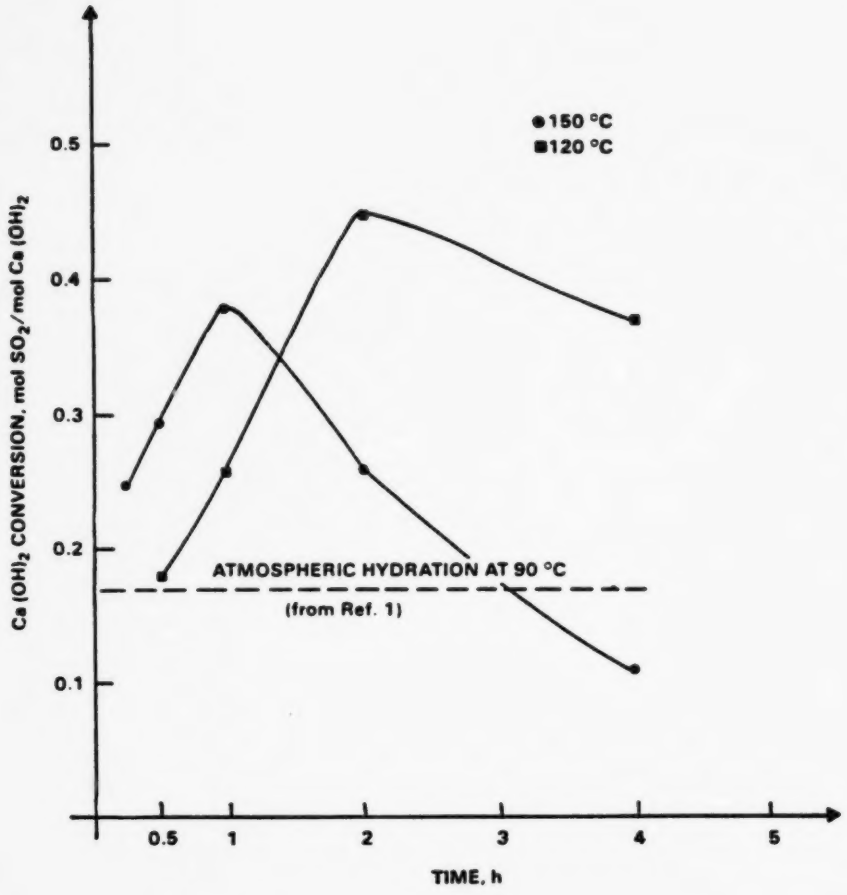

Figure 5. Combined time and temperature effects of pressure hydration on the reactivity of sorbent prepared at the weight ratio of flyash to $Ca(OH)_2$ of 1:1 (sand-bed reactor conditions the same as in Figure 3).

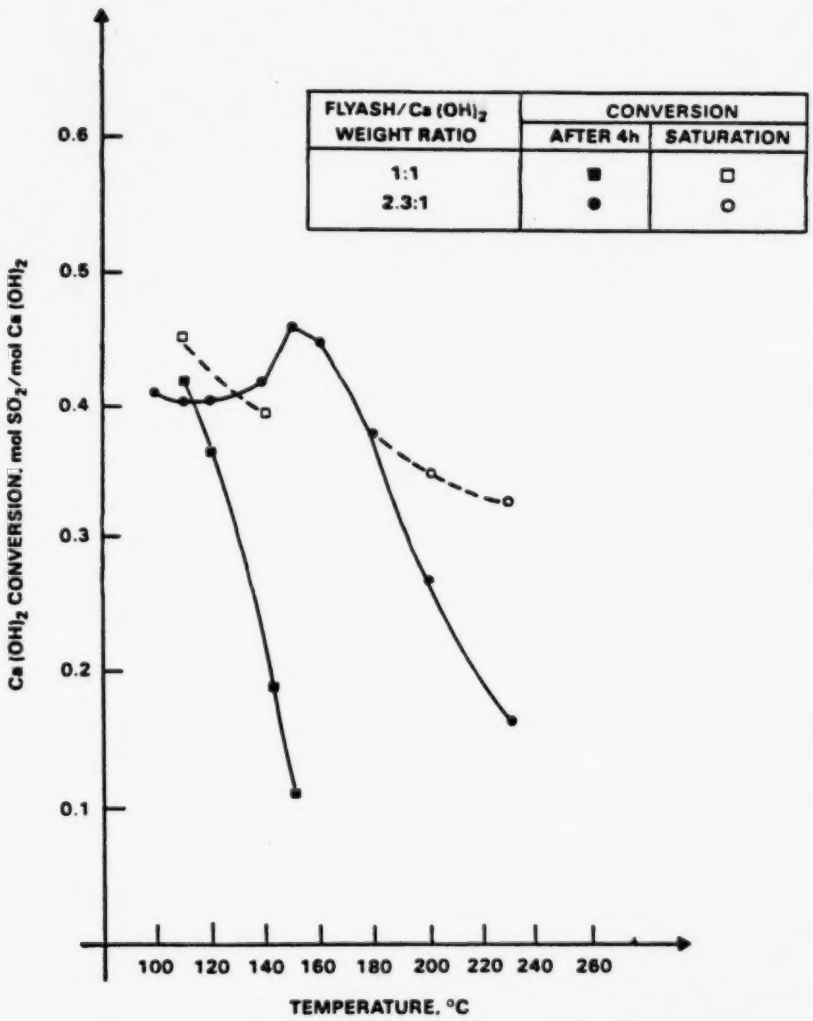

Figure 6. The effect of temperature of pressure hydration on the reactivity of flyash/$Ca(OH)_2$ sorbents (sand-bed reactor conditions the same as in Figure 3).

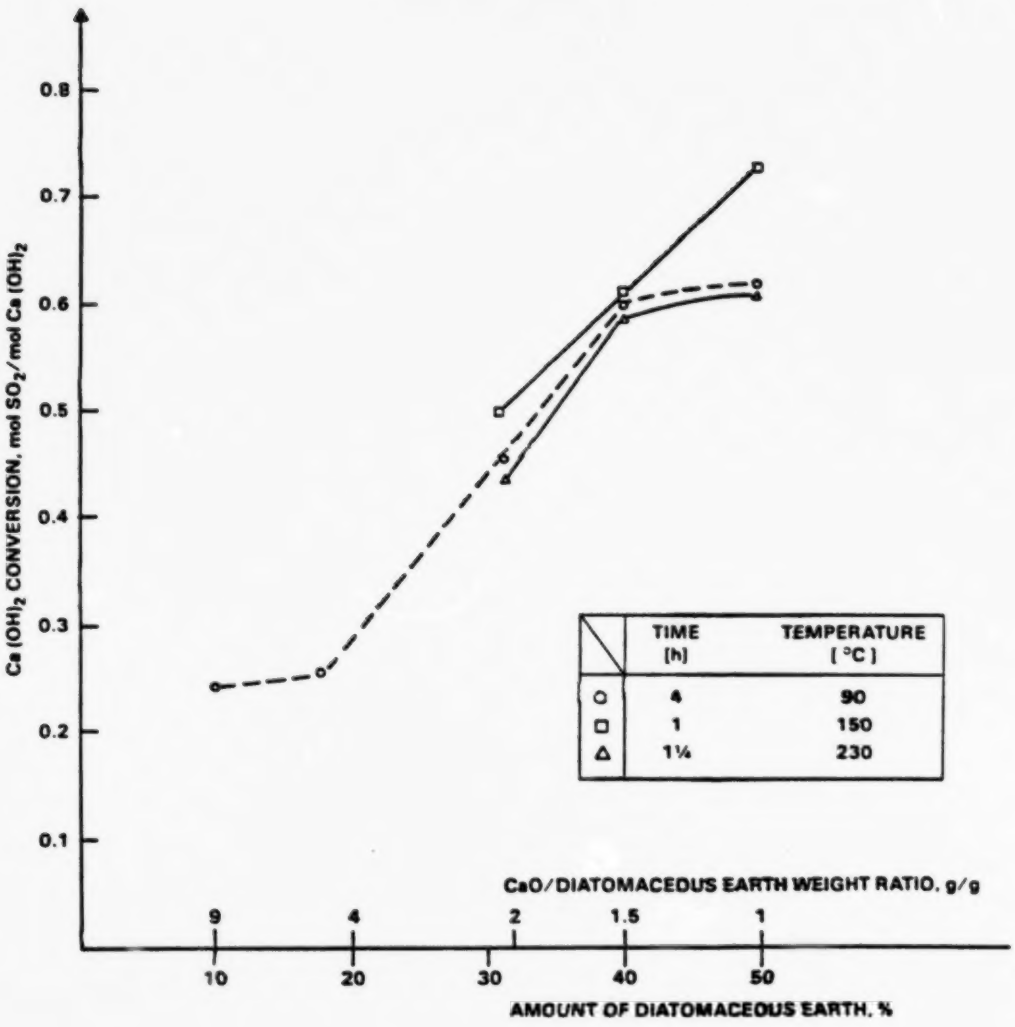

Figure 7. Combined effects of the temperature of pressure hydration and weight ratio of diatomaceous earth to CaO on the reactivity of the sorbent [sand-bed reactor conditions: relative humidity 60%, temperature 64°C (147°F), SO_2 concentration 1000 ppm].

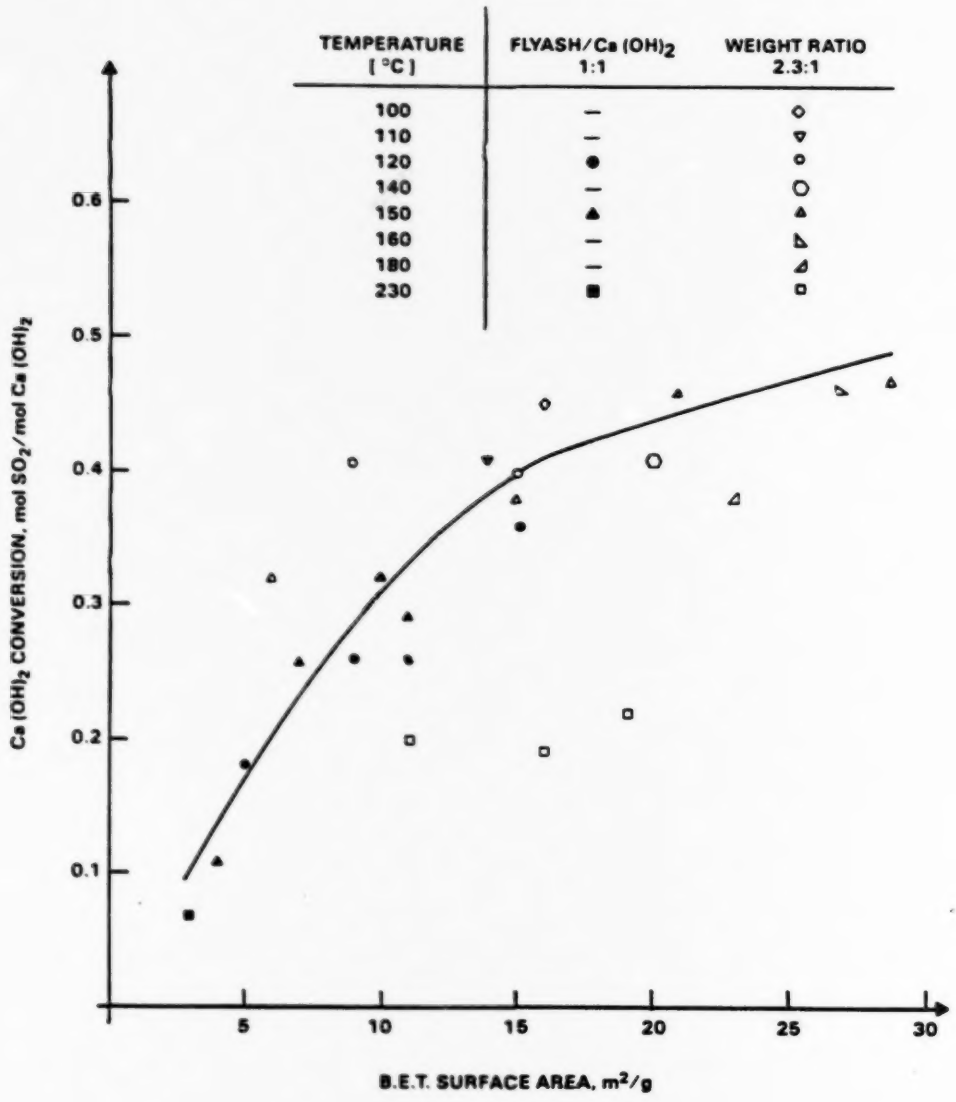

Figure 8. Correlation between measured B.E.T. surface area and the reactivity of flyash/$Ca(OH)_2$ samples (sand-bed reactor conditions the same as in Figure 3).

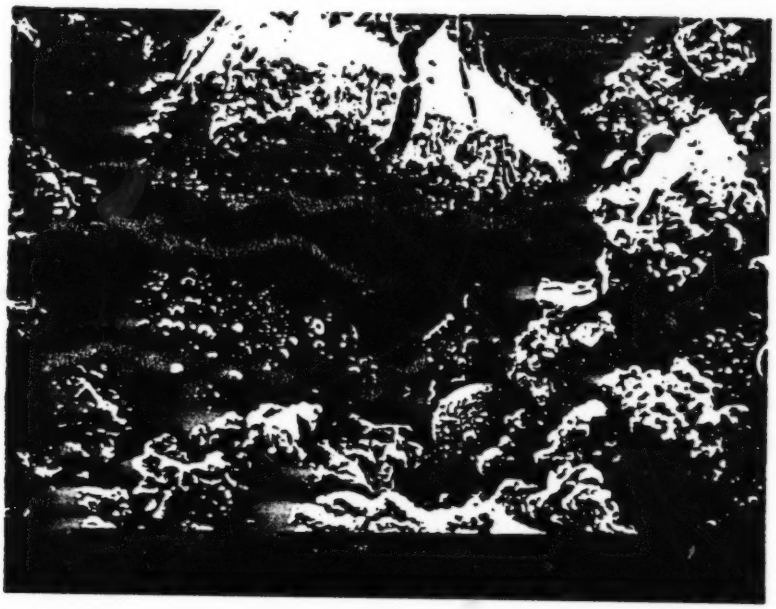

Figure 9. SEM photograph of sorbent at a weight ratio of flyash to $Ca(OH)_2$ of 2.3:1, pressure-hydrated at 150°C (302°F) for 15 min. (x2000).

Figure 10. SEM photograph of sorbent at a weight ratio of flyash to $Ca(OH)_2$ of 2.3:1, pressure-hydrated at 150°C (302°F) for 4 h (x5000).

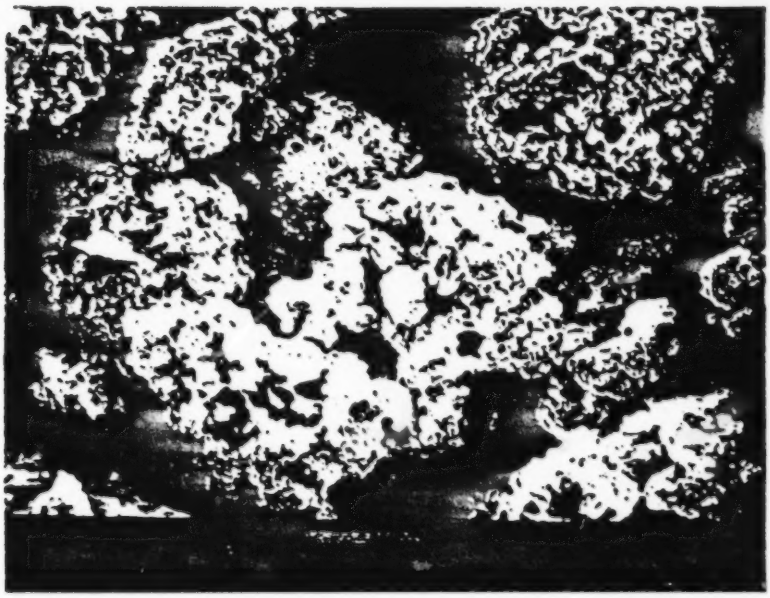

Figure 11. SEM photograph of sorbent prepared at a weight ratio of flyash to $Ca(OH)_2$ of 2.3:1, pressure-hydrated at 230°C (446°F) for 4 h (x2000).

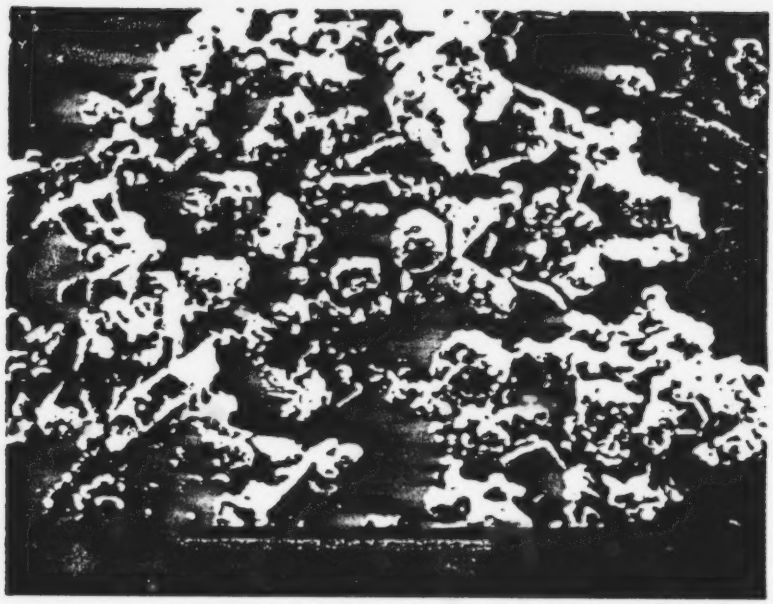

Figure 12. SEM photograph of sorbent prepared at a weight ratio of flyash to $Ca(OH)_2$ of 1:1, pressure-hydrated at 150°C (302°F) for 4 h (x5000).

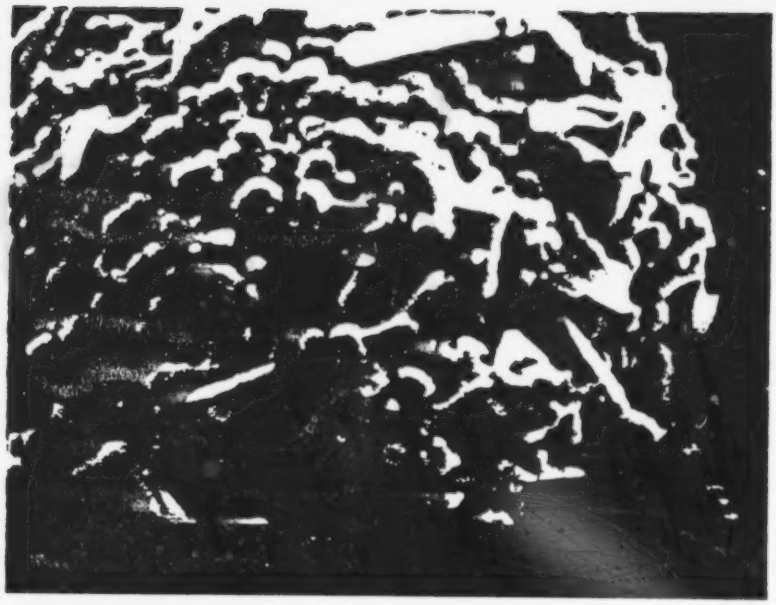

Figure 13. SEM photograph of sorbent prepared at a weight ratio of flyash to $Ca(OH)_2$ of 1:1, pressure-hydrated at 150°C (302°F) for 4 h (x10000).

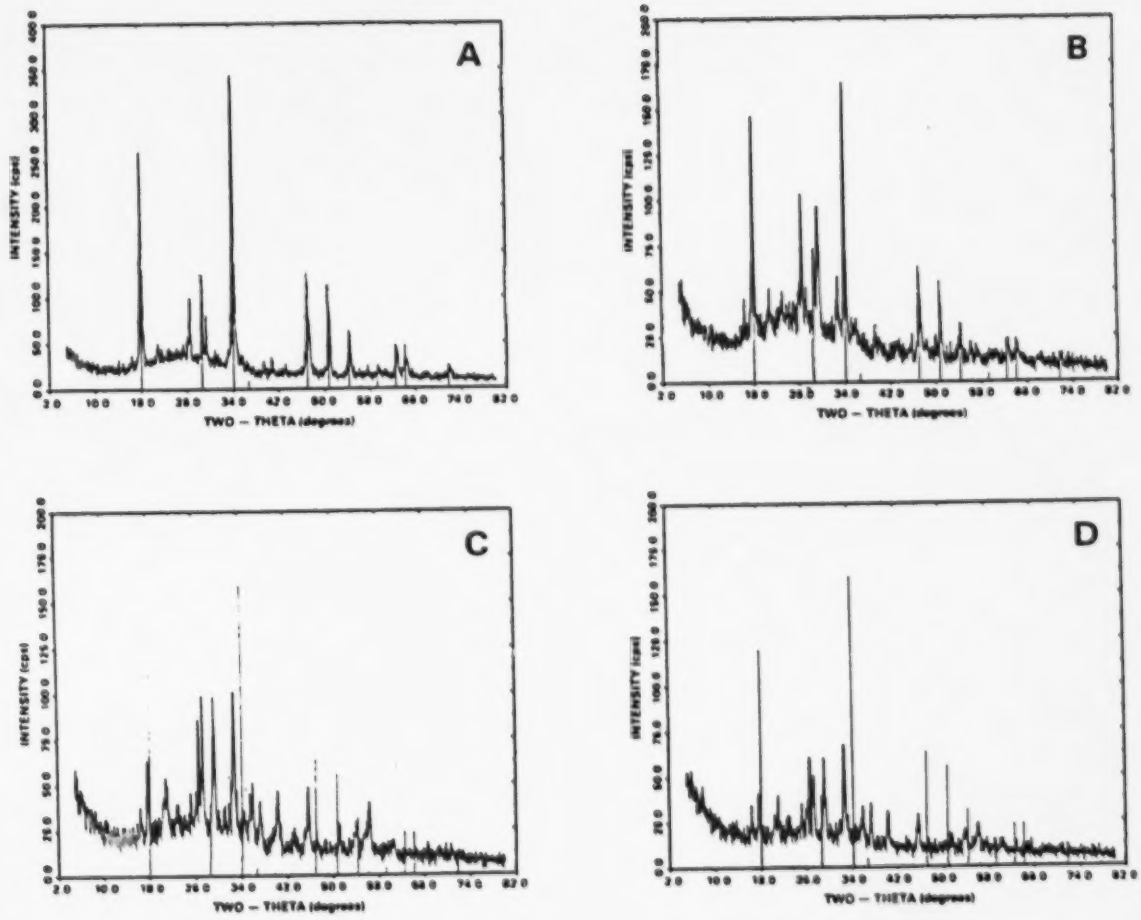

Figure 14. X-ray diffraction patterns of sorbents at the weight ratio of flyash to $Ca(OH)_2$ of 2.3:1; A - dry mixed, B - 150°C (476 kPa) [302°F (69 psi)] for 0.5 h, C - 150°C for 4 h, and D - 230°C (2793 kPa) [446°F (405 psi)] for 4 h.